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Infrared spectroscopic group analysis of solid aromatic multicomponent mixtures

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Summary

The methods of sample preparation for infrared spectroscopy of solids are discussed. A quantitative calculation of error as a function of sample homogeneity is described. Increments for determining structural groups in aromatic solids mixtures are calculated on the basis of infrared spectra of aromatic substances, e.g. methyl groups at 1380 cm^{-1} and aromatic CH groups in the region of 910-650 cm^{-1}. A method of almost completely determining carbon distribution into various groups is described. The results obtained for three seam coals from the Ruhr region are used as examples of application.

Problems of quantitative infrared spectroscopy of solids

Where the aim is direct quantitative evaluation of infrared spectra via known absorption coefficients or calculatory increments obtained therefrom, the reliability of the quantitative evaluation of measurements has to be assured. Before dealing in detail with the potential sources of error we will briefly discuss the methods of sample preparation.

1. Thin sections or ground thin sections. What speaks against using this method for quantitative measurements is the fact that determining exact cell thickness is difficult and that the substances themselves may change even during sample workup.

2. Suspensions in a low-absorption solvent. This method, too, is hardly suitable for quantitative measurements since thickness and concentration cannot be determined with sufficient accuracy.

3. Fine dispersion of substance to be analyzed in potassium bromide. The KBr method developed by SCHIEDT & RHEINWEIN [19] and by STIMSON & O'DONNEL [20] can be used for quantitative spectrum evaluation if preparation techniques are suitable.

The correlation between measured value and concentration to be determined, required for quantitative measurement, is expressed by the Beer-Lambert law. For evaluation at band maximum

$$\log (I_0/I) = E = a \cdot c \cdot d = a \cdot f$$

where I_0/I = percent transmittance of background or band at maximum
- E = extinction
- a = maximum absorption coefficient (cm^2/g)
- c = concentration (g/mL)
- d = thickness (cm)
- f = area concentration (g/cm^2)

For integration of a band area between the wavenumbers ν_1 and ν_2 (cm^{-1})

$$\int_{\nu_1}^{\nu_2} \log (I_0/I) \cdot d\nu = B \cdot c \cdot d = B \cdot f$$

B = integral absorption coefficient (cm/g)

The quantity f can be defined as the quantity of substance behind an irradiated area element.

Each absorption coefficient belongs to a specific wavenumber (wavenumber range) and a specific bond type of the atoms involved in the vibration. The results obtained with the aid of this relationship may be adulterated by various factors. The deviations in extinction caused by errors of measuring I_0/I and d are discussed in detail by various authors, among them MARTIN [16]. With errors of 1% each for I_0, I, or d, the deviations for measured transmittances of 10-60% are generally below 2% for the calculated extinctions. We assume here, however, that the substance to be analyzed is dispersed completely uniformly over the irradiated area and disregard intensity fluctuations caused by stray light and reflection. The extent to which these factors may affect the analysis of solid substances in KBr pressed pellets will be discussed below.

In the KBr pellet technique we cannot be completely certain that the substance in question will be dispersed completely uniformly. Inhomogeneities may occur in three different forms:

A. In coarse distribution, the substance particles in the pellet are very large.

B. Some areas of the pellet do not contain any sample substance.

C. The substance in fine-grained form is distributed throughout the entire pellet but inhomogeneously.

In case A, light of wavelength ν_1 and intensity I_0 may encounter a large substance particle and drop to a value of zero already after passing through leg a (Figure 1).

Leg b through the particle then no longer affects absorption. If the entire irradiated area is filled with particles of diameter a + b, total I will be zero; if, however, particles of diameter a + b occur only in certain areas and the remaining areas contain only particles with diameters of much less than a, the extinction calculated from a measured value of I is too small for the number and diameter of particles with diameter greater than a.

For bituminous coals it was found that case A becomes important only for particles larger than 30 μ.

Case B means that in some areas of the pellet no energy is absorbed. It has been discussed theoretically by JONES [11]. According to him, the measured extinction relative to the expected one decreases with increasing extinction and with increasing area lacking substance particles. JONES' calculations showed that for instance at 10% substance-free pellet area and an extinction of 0.55, the extinction error is already as high as 10%.

Case C, the most frequent case and one that is exceedingly likely in infrared spectroscopy, means that, although all pellet areas contain substance particles and particle size is constant or varies within narrow limits, the area concentration is inhomogeneous on account of unequal distribution of sample substance or varying thicknesses. Such variations in thickness occur if in a cell for liquids the windows are not exactly plane-parallel. The inhomogeneous distribution in a pellet with plane-parallel windows can be represented schematically (Figures 2a and 2b). Figure 2a shows the substance distribution in the pellet.

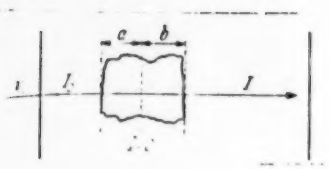
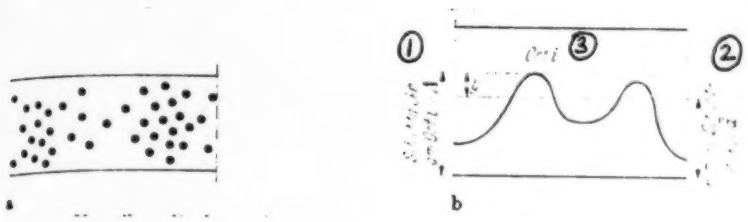


Figure 1. Passage of light through a substance particle



Figures 2a and 2b.

a - distribution in pellet with plane-parallel windows
b - inhomogeneity of thickness

Key: 1 - thickness at point i
2 - mean thickness
3 - point i

If all particles are assumed to gravitate towards a boundary area and there to form a continuous layer, the inhomogeneity of cell thickness develops as represented in Figure 2b.

JONES already pointed out that inhomogeneous distribution of the sample substance in the pellet is possible. In the following we discuss this problem from a theoretical standpoint; the possible extinction errors have been calculated.

The transmittance ($\bar{D}$) measured at inhomogeneous distribution, i.e. unequal thickness, being greater than that of a mean thickness (D^*) with homogeneous substance distribution is a reflection of the fact that the effect to be discussed exists. Let the inhomogeneity be symmetrical, i.e. the sum of all positive and negative deviations from mean thickness be zero. If we assume that extinction could be measured directly, the total extinction calculable from thicknesses at all points would be equal to the thickness of a mean layer of homogeneous distribution. This can be proved by using a Gaussian distribution curve.

Spectrometers, however, linearly record transmittance rather than extinction. Thus it is mean transmittance ($\bar{D}$) that we have to consider, taking into account thickness distribution and again using a Gaussian distribution curve. The following equations then apply:

$$\bar{D} = \frac{1}{\sigma\sqrt{2\pi}} \cdot \int_{(-\infty)}^{(+\infty)} D_\lambda \cdot e^{-\frac{y^2}{2}} \cdot d\lambda$$

D_λ = transmittance at point

$D_\lambda = e^{-2{,}3026 \cdot \varepsilon \cdot c \cdot \lambda}$

$k = 2{,}3026 \cdot \varepsilon \cdot c$

$D_\lambda = e^{-k \cdot \lambda}$

and

$$y = \frac{\lambda - \bar{d}}{\sigma} \qquad \lambda = \sigma y + \bar{d} \qquad d\lambda = \sigma \cdot dy$$

By substitution we get

$$\bar{D} = \frac{\sigma}{\sigma\sqrt{2\pi}} \cdot \int_{(-\infty)}^{(+\infty)} e^{-k \cdot \lambda} \cdot e^{-\frac{y^2}{2}} \cdot dy$$

where $1 = \sigma y + d$

and it follows from the transformation of the limits of integration that $D = \frac{1}{\sqrt{2\pi}} \cdot e^{-k \cdot d} \int_{(-\infty)}^{(+\infty)} e^{-k \cdot \sigma \cdot y} \cdot e^{-\frac{y^2}{2}} \cdot dy .$

By substituting the transmittance of the homogeneous mean layer $D^* = e^{-k \cdot \bar{d}}$ we get in exponential designation:

$$\bar{D} = \frac{D^*}{\sqrt{2\pi}} \int_{(-\infty)}^{(+\infty)} \exp\left[-k \cdot \sigma \cdot y - \frac{y^2}{2}\right] \cdot dy .$$

By transformation we get

$$\bar{D} = \frac{D^*}{\sqrt{2\pi}} \int_{(-\infty)}^{(+\infty)} \exp\left[\frac{1}{2}(y^2 + 2k \cdot \sigma \cdot y + K^2 \cdot \sigma^2) + \frac{1}{2}(k^2 \cdot \sigma^2)\right] \cdot dy$$

$$= \frac{D^*}{\sqrt{2\pi}} e^{\frac{k^2\sigma^2}{2}} \int_{(-\infty)}^{(+\infty)} \exp\left[-\frac{1}{2}(y + k \cdot \sigma)^2\right] \cdot dy .$$

For $y + k \cdot \sigma$ the auxiliary variable z is introduced. Since $k \cdot \sigma$ is constant, $dz = dy$ and thus

$$\bar{D} = \frac{D^*}{\sqrt{2\pi}} \cdot e^{-\frac{k^2\sigma^2}{2}} \cdot \int_{z(-\infty)}^{z(+\infty)} e^{-\frac{z^2}{2}} \cdot dz .$$

The value of the integral is $\sqrt{2\pi}$ and thus

$$\bar{D} = D^* \cdot e^{\frac{k^2\sigma^2}{2}}$$

Since $k^2\sigma^2$ is positive, $\bar{D}$ must be greater than D^*. For very great values of $(k^2\sigma^2)/2$, $\bar{D}$ might formally be greater than 1. This, however, would be illogical in physical terms since in that case, on account of the great σ, integration would be over a considerable number of negative thicknesses.

At a standard deviation of $\sigma = 33\%$, i.e. at $\bar{d}/\sigma = 3$, an apparent $\bar{D}$ greater than 1 would occur only at extinctions above 7.6. The above development was programmed with the variables Δ, E, and σ (Δ and E over one ten-step decade each; σ in 17 steps from zero

to $\frac{J_{max}}{\sigma} = 3$) for calculating transmittance (D), extinction (E) or ($\overline{E}$), and relative extinction error $\left(\frac{\overline{E} - E}{E} \cdot 100\right)$ in algol. The results of this calculation have been represented in Figure 3. According to them, the relative extinction error is less than 1% for example at a relative standard deviation of cell thickness of 10%, and up to extinctions of 0.8. However, errors can be considerable at high standard deviations of thickness.

We used two methods of determining which standard deviations of thickness can occur for coals pressed into KBr pellets.

I. Determining coal particle size in the pellets by microscopy.

II. Determining homogeneity of distribution by microphotometry.

I. Since the microscopic examination of pellets proved unsuitable, the coal particles were removed from the pellets and examined under the microscope. The following results were obtained with respect to coal samples ground for different periods of time.

Grinding time: 5 min - dominant particle size 5-10 μ; 15 min - predominant particle size 2-3 μ, also particles smaller or larger than that; 30 min - similar to grinding time of 15 min; 60 min - predominant particle size 1-2 μ, also particles smaller or larger than that; 480 min - most particles with diameter around 1 μ, no smaller particles detected.

II. Another possibility of assessing the homogeneity of coal particle distribution in pellets is determining the transmittances of small pellet area regions microphotometrically. Even if the composition of particles of a certain coal in the pellet were to vary, it can be assumed that the mean absorption coefficients of the particles in the visible region are approximately the same. If we go on to assume that the distribution in the pellet does not vary overly much, it appears plausible for the trans-

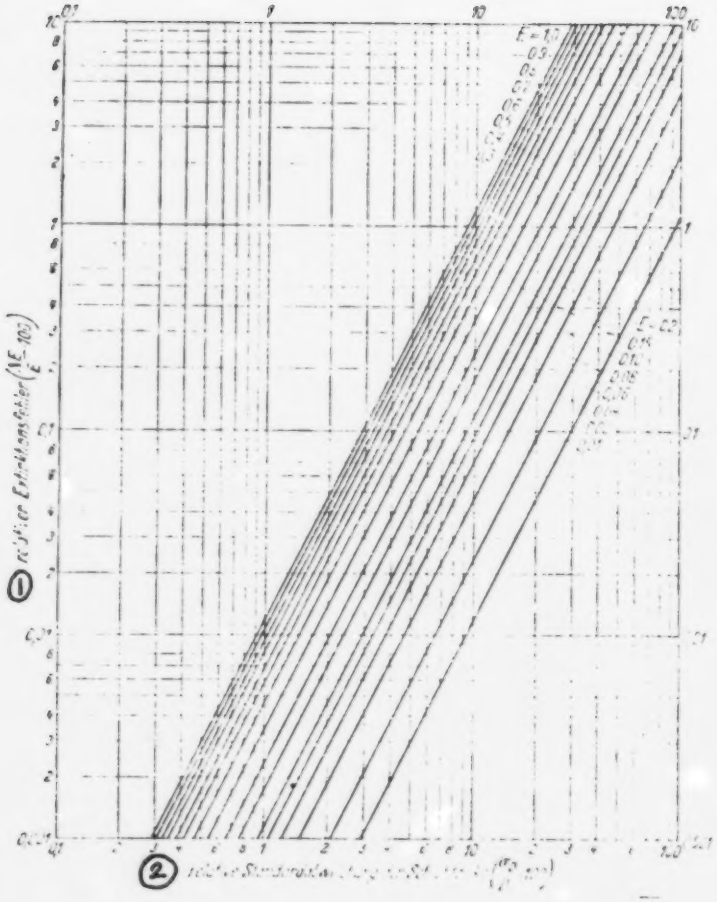


Figure 3. Extinction errors of inhomogeneous thicknesses

Key: 1 - relative extinction error
2 - relative standard deviation of thickness

Translator's note: In Figures and Tables, where applicable, please read commas as decimal points.

mittances measured for certain area regions to be proportional to the respective average coal thicknesses.

KBr pellets of suitable concentration were pressed from mixtures of various coals, from solid coal extracts, and from model substances. The transmittances of pellet areas of 3·100 μ were measured. By suitable shifting of the stage, 150 adjacent ranges with a total area of 100·450 μ were examined. In only a few cases the photometer permitted stopping out even smaller ranges. At a range width of 3 μ it can be assumed with sufficient certainty that differences exist in the concentrations of the coal particles in question. The length of the range - 100 μ - , however, already resulted in a certain degree of averaging. The standard deviations calculated from groups of 150 measured values each and the relative extinction errors to be expected for them according to Figure 3 have been listed in Table 1.

The resultant extinction errors are insignificant. Since the concentrations used for these studies are considerably lower than those in pellets for infrared spectroscopy, the distribution in the latter will be even more favourable.

The effects of grinding time were studied in the same manner on coal samples (K 22). These studies, too, show that extinction deviations are insignificant, but that, as is apparent from Figure 4, grinding time is without influence only from approx. 60 min upwards. Findings by other authors, e.g. BARNES et al. [1], were similar.

We also determined experimentally whether stray light at longer wavelengths has an appreciable effect on infrared spectral data of coal/KBr pellets.

For this purpose, mixtures of coal and KBr obtained after different grinding times were pressed into high-concentration pellets with an average thickness of 0.31 cm. The concentrations were

Table 1. Photometric determination of thickness inhomogeneities

Substanz (1)	Konzentration im 300 mg-Preßling ($g/cm^2 \cdot 10^5$) (2)	Standardabweichung der Durchlässigkeit (in % vom Mittelwert) (3)	Relativer Extinktionsfehler für eine angenommene $E = 0{,}5$ % (4)
Kaliumbromid (5)	(0)	2,9	0,05
Chinizarin (6)	6,17	2,2	0,03
2-Methyl-naphthalin (7)	10,85	4,2	0,10
Phenanthrenchinon (8)	3,05	3,9	0,09
Tetrahydrocarbazol	3,62	1,3	0,01
5,12-Dihydro-tetracen	3,60	4,6	0,12
Kohle K 22 (9)	4,82	2,2	0,03
Kohle K 41	5,79	5,1	0,15
(10) Schockerhitzte Kohle K 15	5,12	4,0	0,09
Schockerhitzte Kohle K 34	5,55	2,2	0,03
Exinit (Zollverein)	3,92	3,4	0,07
Vitrinit (Zollverein)	4,01	2,8	0,05
(11) Pyridinextrakt aus Kohle K 23	4,85	2,5	0,04
Pyridinextrakt aus Kohle K 28	4,08	4,9	0,13
(12) Chloroformextrakt aus K 19	6,04	1,9	0,02
(10) Schockerhitzte Kohle K 28	6,36	3,6	0,07

Key:

1 - substance
2 - concentration in 300-mg pellet
3 - standard deviation of transmittance (in % of mean value)
4 - relative extinction error for assumed E = 0.5
5 - potassium bromide
6 - quinizarin
7 - 2-methylnaphthalene
8 - phenanthrenequinone
9 - coal K 22/K 41
10 - shock-heated coal K 15/K 34
11 - pyridine extract from coal K 23/K 28
12 - chloroform extract from coal K 19

Zollverein = name of coal mine

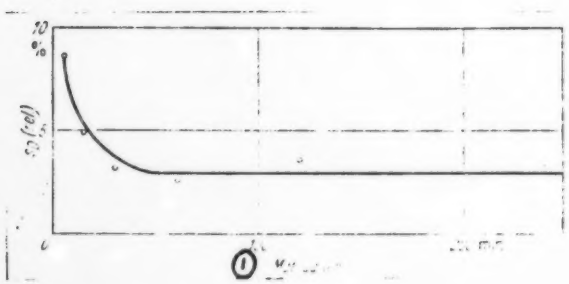


Figure 4. Relative deviation of photometrically measured transmittance of coal (K 22)/KBr pellets as a function of sample grinding time

Key: 1 - grinding time

Table 2. Distortions of absorption caused by stray light and measured infrared spectroscopically on KBr pellets with coal K 23,8

MahlDauer (1)	Flächenkonzentration / (g/cm²) (2)	Streustrahlung in % Durchlässigkeit bei cm^{-1} (3)		
		2920	1590	750
1	0,53	0,5	0,7	3,0
5	0,53	0,5	0,7	1,8
15	0,58	0,3	0,3	0,8
30	0,62	0,3	0,3	0,8
60	0,62	0,2	0,2	1,3
240	0,62	0	0	1,0
480	0,56	0	0	1,0

Key: 1 - grinding time
2 - area concentration
3 - stray light in % transmittance at cm^{-1}

chosen on the one hand so as to have extinctions of formally at least 10 at weak bands and on the other hand so as to achieve low transmittance in regions of maximum transmittance with suitable spectrometer adjustment and recording. Under these conditions the distortions of absorption caused by stray light are measured as apparent transmittance in the spectral regions of interest. Table 2 lists the pertinent values.

At grinds of more than 60 min the stray light effect is negligibly small.

Reflectance losses on pellet surfaces were compensated by using pure KBr pellets in the spectrometer reference beam. The reflectance loss (R) at the coal particles imbedded in KBr can be calculated approximately according to

$$R = 2 \cdot \left(\frac{n - n_1}{n + n_1} \right)^2$$

where n = refractive index of KBr, n_1 = refractive index of coal. If a refractive index of 1.9 is used for coals, R is less than 2%. Reflectance losses are not appreciably affected by changes in irradiated wavelength.

It appeared from these basic reflections that a direct quantitative evaluation of infrared spectra of coals or similar substances pressed into KBr pellets would be meaningful. We still needed to determine the conditions of sample preparation. Further above we mentioned that a correlation existed between cell thickness inhomogeneity, and thus extinction error, and grinding time. It was plausible to expect this correlation to be reflected also in the absorption coefficients calculated from coal infrared spectra. To clarify this point, K 24 coal samples were ground with KBr for different periods of time. Several pellets of different concentrations were pressed from each mixture. Figure 5 is a plot of mean absorption coefficients of several bands, determined from

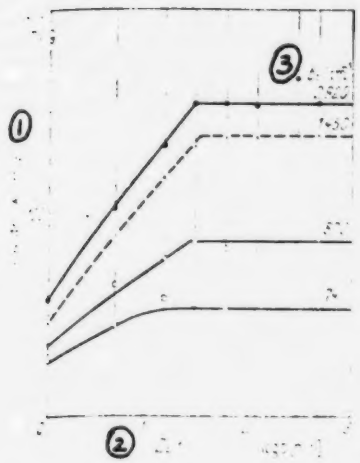


Figure 5. Correlation between maximum absorption coefficients calculated from infrared spectral data of coal (K 24)/ KBr pellets and grinding time during sample preparation

Key: 1 - maximum absorption coefficient
2 - time
3 - at cm^{-1}

spectral data, over grinding time. The absorption coefficients are independent of grinding time from about 30 min for weak bands, from about 60 min for strong bands. As a result, a grinding time of 480 min was used for all infrared spectroscopy described in this paper.

According to the Beer-Lambert law, extinction plotted over area concentration should produce a straight line passing through zero the slope of which corresponds to the absorption coefficients. The fact that this is indeed so has been demonstrated by various authors, for instance KIRKLAND [13,14] for various substances, BROWNING et al. [3] for atropine and scopolamine, and ROSENKRANTZ et al. [18] for various hormones, but we know of no detailed study of this question for coals. To try and provide an answer ourselves we pressed KBr pellets containing one coal or one coal extract at different mixing ratios and calculated the maximum absorption coefficients for the three bands at 2920 cm^{-1} (background of 3125-2550 cm^{-1}), 1600 cm^{-1} (background transmittance at 1780 cm^{-1}), and 870 cm^{-1} (background transmittance at 920 cm^{-1})..The scatter was as shown in the Table below:

	① Relative Streuung des maximalen Absorptionskoeffizienten der Bande bei (cm^{-1})		
	2920	1600	870
Kohle (K 24) ②	2,7%	8,0%	6,4%
Chloroformextrakt aus ③ schockerhitzter Kohle (K 24)	2,7%	8,1%	6,7%

Key: 1 - relative scatter of maximum absorption coefficients of bands at (cm^{-1})
2 - coal (K 24)
3 - chloroform extract from shock-heated coal (K 24)

In view of the above findings a quantitative evaluation of infrared spectral data of coals and similar substances would appear useful if the absorption coefficients at various concentrations have been shown to be reproducible.

Spectroscopy of calibrating substances

What can the spectroscopy of a complex mixture like coal be expected to yield? It can be used to obtain sufficiently significant statistical data on the occurrence of certain chemical structural groups. Since in most cases it is not possible to separate a mixture completely into its individual constituents and to identify the latter, statistical group analysis is the most suitable method of determining chemical structure. In the preceding chapter it has been shown that spectral coal data can be evaluated quantitatively. To calculate from these data the proportions of certain structural groups we need group-specific calculatory increments, which also has been mentioned above. - In some cases these calculatory increments can be calibrated for by means of data obtained with other analytical methods for the same substances, but of course only if sufficiently accurate analytical data are available. The other method, the one we have chosen here, involves developing the calculatory increments from measurements of model substances of known structure.

For the problem at hand the following spectral regions appear potentially suitable for quantitative evaluation:

the region of 3600-2900 cm^{-1} for determining hydroxyl groups;

the bands at 3030, 2920, and 2850 cm^{-1} for determining variously bonded CH groupings;

the band at 1600 cm^{-1} within the limits of 1540-1640 cm^{-1} for determining aromatic carbon or certain carbonyl groups;

the band at 1380 cm^{-1} for determining methyl groups;

the region of 910–650 cm^{-1} for determining aromatic CH groups.

For these regions statistically significant intensity increments of the various structural groups in the molecule shall be determined from measurements with a number of suitable model substances. The latter were selected on the basis of the following assumptions which are in accordance with current knowledge of bituminous coals.

1. The carbon skeleton consists essentially of aromatic and hydroaromatic rings. Except for methyl groups there are no appreciable fractions of paraffinic groups. Aromatics may occur as various ring systems but do not contain more than four condensed rings.

2. A large part of the oxygen occurs in the form of phenolic hydroxyl groups, but some oxygen is present also in quinoid carbonyl groups or carbonyl groups conjugated with the aromatic skeleton, as well as in predominantly cyclic ethers.

3. Nitrogen and sulphur occur mainly in heterocyclic form.

More than 100 pure substances selected in accordance with the above assumptions were examined; most of them came from bituminous coal tar. The mean composition of all substances - 84.9% C, 6.3% H, 7.9% O, 0.6% N and 0.3% S - was approximately that of a gas coal; the mean molecular weight was about 200.

In order to derive suitable calculatory increments for the various structural groups from the data obtained for these model substances, these data are determined for the respective molecular fraction x_i of each group.

$$x_i = \frac{z_i \cdot G_i}{M}$$

where z_i = number of groups i in molecule

G_i = weight of group i

M = molecular weight

The increment of an absorption coefficient of a group i thus is

$a_{z_i} = \frac{a}{z_i}$ for maximum evaluation and

$B_{z_i} = \frac{B}{z_i}$ for integral evalution.

Determining increments for hydroxyl groups in the region of 3600-2900 cm^{-1}

To determine an increment $B_{x_{OH}}$ the integral absorption coefficients measured in the region of 3600-2900 cm^{-1} over the background at 3700 cm^{-1} can be used. The long-wavelength side was corrected in that the uninterrupted course of the hydroxyl group band was extended below the CH stretching bands. Since the hydroxyl band was always considerably stronger the error potential was small.

19 substances with phenolic hydroxyl groups without interfering adjacent groups give an increment of $15.5 \cdot 10^5$ (cm/g OH) with a relative scatter of $\pm$ 17%. Three substances with hydroxyl groups in saturated structures give a mean value of $10.2 \cdot 10^5$; three other substances with methyl groups immediately adjacent to the phenolic hydroxyl groups give a mean value of $9.7 \cdot 10^5$; and two substances with quinoid carbonyl groups adjacent to the phenolic hydroxyl group give an increment of approx. $5 \cdot 10^5$.

These differences render the direct application of any one of the increments unsuitable for coal analysis since there is no certainty on which groups lie adjacent to phenolic hydroxyl groups

in coals. Moreover, the above-mentioned fact that entrained water or stray light losses may introduce errors already reduces the reliability of data obtained for this region.

Determining increments in the CH stretching region

In the region around 3000 cm^{-1} the maximum extinctions of the CH stretching bands above the base line between 3160 and approx. 2500 cm^{-1} were evaluated. 22 substances gave a mean increment of $a_{x_{CH}} = 1.55 \cdot 10^2$ (cm/g CH) with a relative scatter of $\pm$ 10%. Eight other substances gave considerably higher values, presumably on account of overlaying OH bands or of other CH bands. This fact as well as possible errors caused by stray light reduce data reliability.

The substances absorbing at 2920 cm^{-1} can be divided into two groups. 12 substances substituted only by methyl groups gave an increment of $a_{x_{CH(CH_2)}} = 1.94 \cdot 10^2$ (cm^2/g CH) with a relative scatter of $\pm$ 40%. 12 substances containing only methylene and methine groups gave an increment of $a_{x_{CH(CH);CH)}} = 2.55 \cdot 10^2$ (cm^2/g CH) with a relative scatter of $\pm$ 40%. These results are unsatisfactory. It is doubtful whether our assumption of methylene groups in different types of substances having the same increments is correct. FRANCIS [8] as well as HASTINGS et al. [10] showed for example for liquid hydrocarbons that the relationships are more complex and that there is no common increment for different methylene groups. FRANCIS, for instance, observed that at 2920 cm^{-1} the methylene group in cyclohexyl rings had a calculatory increment that was greater by a factor of 1.2 than that of paraffinic methylene groups, greater by a factor of 3.0 than that of methylene groups in cyclopentyl rings, and greater by a factor of 3.3 than that of methyl groups.

The fact that the above restricting factors were observed and that stray light may cause errors renders this region unsuitable for direct quantitative evaluation.

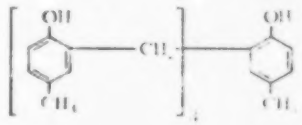
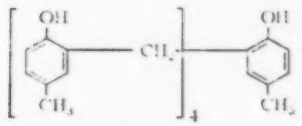
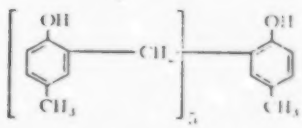
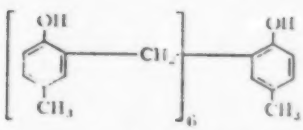
Evaluation of aromatic band at 1600 cm^{-1}

The band at 1600 cm^{-1} is evaluated integrally within the limits 1640-1540 cm^{-1}, reference background being maximum transmittance at approx. 1800 cm^{-1}. 42 substances containing neither phenolic nor quinoid oxygen, when related to aromatic carbon, gave a mean increment $B_{xCar} = 5.4 \cdot 10^3$ (cm/g C) with a relative scatter of $\pm$ 44%. 14 substances with phenolic oxygen gave an increment $B_{xC_{ar}} = 1.95 \cdot 10^4$ (cm/g C) with a relative scatter of $\pm$ 13%. The situation for dioxynaphthalenes is obviously unusual. Six substances of this type gave an increment $B_{xC_{ar}} = 5.23 \cdot 10^4$ (cm/g C) with a relative scatter of $\pm$ 21%. The increments were about the same for quinones. Six substances gave an increment $B_{xC_{ar}} = 5.43 \cdot 10^4$ (cm/g C) with a relative scatter of $\pm$ 9%. Even higher were the increments for substances containing both phenolic and quinoid oxygen in arrangements that make the existence of intramolecular hydrogen bridges likely. Six substances of the hydroxyanthraquinone type gave an increment $B_{xC_{ar}} = 1.01 \cdot 10^5$ (cm/g C) with a relative scatter of $\pm$ 6%.

These findings show that no uniform increment can be expected for this region. On the other hand they could be used for estimating, if the aromatic carbon content was known, whether and how many quinoid carbonyl groups were present.

In the case of condensed aromatic hydrocarbons it was found that increments are generally lower for linearly condensed forms (naphthalene, anthracene) than for angularly condensed forms (phenanthrene). Where only one hydrogen atom in a condensed three-ring system was substituted by a methyl group, the increments were

Table 3. Calculation of increments for CH_3 groups from maximum absorption coefficients of model aromatics in KBr pellets for which spectra were recorded at 1380 cm^{-1}

① Molgewicht	Substanz ②	$a_{\varepsilon CH_3} \cdot 10^{-3}$ (cm^2/g)
122	2,3-Dimethyl-phenol	5,06
122	3,4-Dimethyl-phenol	2,53
136	3,4,5-Trimethyl-phenol	5,63
143	3-Methyl-isochinoline	6,54
156	2,3-Dimethyl-naphthalene	3,37
156	2,6-Dimethyl-naphthalene	4,36
170	1,3,7-Trimethyl-naphthalene	2,70
170	2,3,6-Trimethyl-naphthalene	4,48
172	1-Hydroxy-2,6-dimethyl-naphthalene	4,87
180	2-Methyl-fluorene	2,64
184	2,3,6,7-Tetramethyl-naphthalene	4,71
192	2-Methyl-anthracene	3,84
192	1-Methyl-phenanthrene	3,10
226	Bis-(α Methyl-benzyl) ether	5,14
208	9,10-Dimethyl-9,10-dihydro-anthracene	5,52
214	4,4'-Dihydroxy-diphenyl-1,1-ethane	5,18
238	Diphenyl-tetramethyl-ethane (sym.)	3,42
242	4,4'-Dihydroxy-3-methyl-diphenyl-2,2-propane	3,81
268	4,4'-Dihydroxy-diphenyl-1,1-cyclohexane	4,71
282	n-Eicosane	3,68
470		4,65
591		4,87
712		4,55
833		4,70

$$a_{\varepsilon CH_3} = 4{,}34 \cdot 10^2 \pm 1{,}04 \cdot 10^2 \ (\pm 24\%); \quad a = 4{,}34 \cdot 10^2 \cdot x_{CH_3}$$

ausgelassene Substanzen ③

1,2,4,5-Tetramethyl-benzene	1,41
2,5-Dimethyl-phenol	1,50
2-Methyl-1,4-naphtho quinone	27,26
4,4'-Dihydroxy-diphenyl-methyl-phenyl-methane	13,69
4,4'-Dihydroxy-3,3'-dimethyl-diphenyl-methane	11,79

Key: 1 - molecular weight
2 - substance
3 - omitted substance

considerably higher than for the parent substances (anthracene - methylanthracene) (phenanthrene - methylphenanthrene). These differences, however, shall not be discussed any further here.

Evaluation in the regions of 1540-1400 and 1400-920 cm^{-1}

No meaningful correlation could be established between intensity and the molecular proportion of a structural group for the intense band at 1450 cm^{-1} and for the region of 1400-920 cm^{-1}. The correlation with other parameters will be discussed elsewhere.

Determining methyl group increments from absorption at 1380 cm^{-1}

For the deformation band of methyl groups at 1380 cm^{-1} the maximum absorption coefficient above the base between the two ends of the band at approx. 1400 and 1350 cm^{-1} was determined. 24 substances gave an increment $B_{x_{CH_3}} = 4.34 \cdot 10^2$ ($cm^2/g\ CH_3$) with a relative scatter of $\pm$ 24%. Several substances gave greatly deviating values and were not included in averaging. Moreover, some of the model substances had a maximum or strong side absorption at 1380 cm^{-1} although they did not contain any methyl groups. Of the 24 substances used for increment determination, 19 had the methyl groups directly on the aromatic ring, while in the remaining 5 the methyl groups were linked to other aliphatic groups. The increment values have been listed in Table 3. If the increments of the two groups are examined separately, two mean values are obtained which agree well with the overall mean.

On the whole these findings do not encourage using derived increments for determining methyl groups in coals and similar

substances. However, since position and shape of the relatively weak bands occurring in coal spectra are very constant, the bands might be produced by a certain mean type of methyl substitution and be characteristic of the number of methyl groups involved. This view is corroborated by the systematic nature of data obtained for coals. Even without accurate knowledge of the increments it seems to be possible to estimate methyl group content in the substances to be analyzed.

Recently, TSCHAMLER & RUITER [22] also attempted a quantitative determination of methyl groups from the absorption at 1380 cm^{-1}. They, too, observed considerable scatter of the maximum absorption coefficients of pure substances.

Determining aromatic CH group increments for the region of 910–650 cm^{-1}

The gamma-vibration bands of aromatic CH groups occurring in the region of 910–650 cm^{-1} greatly overlap.

As TSCHAMLER & RUITER [21] were able to show and as will become apparent in the course of the present work, the increments of individual aromatic CH groups in solids do not appreciably depend on the substitution conditions on the aromatic ring. Therefore the entire band complex is evaluated integrally within the limits of 910–650 cm^{-1} above the adjacent point of maximum transmittance at 650 cm^{-1} as reference background. The measurements with 65 substances including a great variety of types gave an increment $B_{x_{CH_{ar}}} = 6.75 \cdot 10^4$ (cm/g CH) with a relative scatter of $\pm$ 12%. Only few substances differed sufficiently from this value to be disregarded. The values have been summarized in Table 4. In the case of the substances used for calculating the mean increment of $6.75 \cdot 10^4$ we see that many of the aromatics with highly polar groups as substituents have higher increments than the

Table 4. Increments of aromatic CH groups for integral absorption coefficients calculated from integral extinctions for model aromatics by infrared spectroscopy in the region of 910–650 cm^{-1}

Molecular weight	Substance	$B_{\Sigma CH_{ar}} \cdot 10^{-4}$ (cm/g)
	2,3-Dimethyl-phenol	6,94
	2,5-Dimethyl-phenol	5,69
	3,4-Dimethyl-phenol	8,72
	3,5-Dimethyl-phenol	8,94
	Indanol2-5	7,56
	3,4,5-Trimethyl-phenol	7,64
	3-Methyl-isoquinoline	6,48
	1-Hydroxy-naphthalene	7,45
	2-Hydroxy-naphthalene	5,36
	Diphenyl	6,21
	1,2-Naphthoquinone	6,33
	Fluorene	6,01
	Carbazol	8,65
	Diphenyleneoxide	7,69
	1,2,3,4-Tetrahydro-carbazol	7,76
171	2,3,6-Trimethyl-naphthalene	5,21
	2-Äthoxy-naphthalene	6,07
	2-Methyl-1,4-naphthoquinone	7,03
	1-Hydroxy-2,6-dimethyl-naphthalene	5,32
	Anthracene	6,79
	Phenanthrene	5,89
	Acridine	6,85
	Phenanthridine	7,26
179	9,10-Dihydro-anthracene	5,69
	4,4'-Dimethyl-diphenyl	5,15
	Benzhydrol	6,16
	4-Benzyl-phenol	7,09
	Dipnenylene sulphide	7,10
	Octahydroanthracene	6,36
	2-Methyl-anthracene	6,06
	1-Methyl-phenanthrene	6,45
	2-Methyl-phenanthrene	6,60
	3-Methyl-phenanthrene	6,24
	Anthrone	6,59
	Xanthone	7,81
	Fluoranthene	7,45
	1,2-Dihydropyrene	6,76
	2-Phenyl-naphthalene	5,56
	Tetrahydro-fluoranthene	7,15
	Anthraquinone	7,60
	Hexahydropyrene	6,84
	Phenanthrenequinone	6,36
	4-(Phenyl-isopropyl)-Phenol	7,19
	1,2-Benzofluorene	6,13
	2,3-Benzofluorene	6,51
	2,3-Benz-diphenylene oxide	7,60
	2,4,2',4'-Tetrahydroxy-diphenyl	8,10

(Table 4 continued)

Molecular weight	Substance	
220	2,5-Diphenyl-furane	8,00
228	4,4'-Dihydroxy-3-methyl-diphenyl-2,2-propane	6,51
228	Triphenylene	6,80
230	5,12-Dihydro-tetracene	6,32
230	1,4-Diphenyl-benzene	7,29
234	1,2-Benz-diphenylene-sulphide	7,32
242	4,4'-Dihydroxy-diphenyl-1,1-butane	8,21
244	Triphenyl-methane	5,75
254	2,2'-Dinaphthyl	6,77
260	Triphenyl-methanol	6,49
268	4,4'-Dihydroxy-diphenyl-1,1-cyclohexane	6,98
282	1,2-Dinaphthyl-ethane	5,49
290	4,4'-Dihydroxy-diphenyl-methyl-phenyl-methan	6,48
304	Biacenaphthyliden	6,59
306	1,3,5-Triphenyl-benzene	5,53
330	9,9'-Difluorenyl	6,58
156	1,1'-Dipyridyl	4,93

$$B_{\text{CHar}} = 6{,}75 \cdot 10^4 \pm 0{,}83 \cdot 10^4 \ (\pm 12\%)$$

Of all the measured substances the following substances

2,3-Dimethyl-naphthalene	4,82
2,6-Dimethylnaphthalene	4,10
2,3,5-Trimethylnaphthalene	3,99
2,3,6,7-Tetramethyl-naphthalene	3,85
4,4'-Dihydroxy-diphenyl-1,1-ethane	9,22
4,4'-Dihydroxy-3,3'-dimethyl-diphenyl-methane	9,91
2,2'-Dihydroxy-diphenyl	9,48

as well as the substances listed in the two continuation tables were omitted +:

A. Dihyroxynaphthalenes (M = 160)

1,3-Dihydroxy-naphthalene	10,02
1,5-Dihydroxy-naphthalene	12,52
1,7-Dihydroxy-naphthalene	12,21
2,3-Dihydroxy-naphthalene	10,17
2,6-Dihydroxy-naphthalene	8,72
2,7-Dihydroxy-naphthalene	11,62
Mean value	$10{,}93 \cdot 10^4$

B. Hydroxyl substituted quinones

240	1,2-Dihydroxyanthraquinone	16,98
240	1,4-Dihydroxyanthraquinone	18,54
240	1,8-Dihydroxyanthraquinone	20,60
256	1,2,6-Trihydroxy-anthraquinone	17,99
256	1,2,7-Trihydroxy-anthraquinone	17,13
	Mean value	$18{,}25 \cdot 10^4$
272	1,2,5,8-Tetrahydroxy-anthraquinone	28,20

+ Translator's note: This is a literal translation of the German term "herausgelassen"; the meaning of the German word is not quite clear.

pure hydrocarbons. If all oxygen-containing substances in this compilation are evaluated separately, they give a mean increment of $7.00 \cdot 10^4$, at a mean oxygen content of 11.4% of the substances in this selection. By contrast, the mean increment obtained from oxygen-free substances is $6.50 \cdot 10^4$. This difference can partly be explained by twisting vibrations of the OH groupings about the CO bond frequently causing absorption that starts at about 840 cm^{-1} and becomes increasingly broader towards 650 cm^{-1} [4], partly by the fact that molecular dipole moments change, primarily due to polar substituents, which may change the absorption coefficient yet more.

Additional bands in this region may occur at high long-chain paraffin contents which, however, do not occur in coals in appreciable quantities either. In view of the favourable scatter for a large number of model substances and of the far-reaching absence of interferences in this region it would appear that using the increment $B_{x\ CH_{ar}} = 6.75 \cdot 10^4$ (cm/g CH) for quantitative determination is sufficiently reliable.

The bands occurring in the region of 910–650 cm^{-1} are called gamma-vibration bands. Their location is due primarily to the position, not the type of substituents. The following regions can be given [2]:

5 adjacent H atoms	690–710 (and 730–770)
4 adjacent H atoms	735–770
3 adjacent H atoms	750–810
2 adjacent H atoms	800–860
1 isolated H atom	840–900

However, the situation usually is much more complex since, as has already been indicated for substances with 5 adjacent H atoms, accompanying bands appear frequently. The key frequencies

listed above have also been reported for polynuclear aromatics [6,7,12,17]. Various authors, for example CANNON [5], have used this general assignment for interpreting coal structure. KOJIMA et al. [15] contend that coals do not contain any structures with 3 or 5 adjacent hydrogen atoms, while HADZI [9] thinks that forms with 5 adjacent hydrogen atoms may be present in coals. A first attempt at a quantitative analysis of various forms of substitution was made by TSCHAMLER & RUITER [21]. They concluded from measurements with nine mononuclear and binuclear methyl and hydroxyl substituted aromatics that the specific absorption coefficients of the various types of substitution (1,2,3 and 4 adjacent hydrogen atoms) are of a similar order of magnitude. They disregarded forms with 5 adjacent hydrogen atoms and did not give any details on the measuring techniques used.

For our present purpose we would first like to examine a fairly large number of model substances under comparable conditions. Table 5 lists the increments related to the respective aromatic CH groups. The following means were established from individual values:

	Zahl der Substanzen (1)	Wellenzahlbereich (cm^{-1}) (2)	Integraler Absorptionskoeffizient der C-H-Gruppe (3) $B_i \cdot 10^{-4}$ (cm/g CH)	Abweichung vom Mittelwert (%) (4)
1.	17	910–840	5,90	+ 10
2.	24	840–780	4,98	– 7
3.	38	780–712	5,35	± 0
4.	2	712–650	4,57	– 14
		(5) Mittelwert:	5,35	

Key: 1 - number of substances
2 - wavenumber range
3 - integral absorption coefficient of CH group
4 - deviation from mean
5 - mean

The columns B_x^2 and B_x^4 in Table 5 also list several substances with three adjacent hydrogen atoms. These substances are, in the case of B_x^2, 1-naphthol ($4.32 \cdot 10^4$) and fluoranthene ($5.40 \cdot 10^4$), in the case of B_x^4, 2,3-dimethylphenol ($4.07 \cdot 10^4$), 1,2-dihydropyrene ($4.07 \cdot 10^4$), and tetrahydrofluoranthene ($6.36 \cdot 10^4$). The mean for these substances is $B_x^3 = 5.00 \cdot 10^4$, thus fits well among the means given above. It appears justified to consider the increments for the four regions as equal for purposes of estimating in first approximation the aromatic hydrogen in the various types of substitution; it must be remembered, however, that the fraction in structures with isolated hydrogen may be estimated slightly too high, that of phenyl rings slightly too low. It is not possible with this division of integration regions to identify structures with three adjacent hydrogen atoms. If the latter occur in considerable numbers, they are included as apparent fractions in structures with two or four adjacent hydrogen atoms. - It should also be noted that the mean value of $5.35 \cdot 10^4$ established here is considerably lower than that of $6.75 \cdot 10^4$ established for all calibrating substances throughout the region 910–650 cm^{-1}. This is due to the fact that for most of the substances only two of four partial regions were evaluated. These unevaluated regions, however, sometimes also show considerable absorption caused by most forms of substitution having several bands in the respective region. If we look at the substances for which three or all four regions were evaluated (2-methylanthracene, 3-methylphenanthrene, 2-methylphenanthrene, 2-phenylnaphthalene, and 2,2'-dinaphthyl) and by means of the increments calculate the mean for the evaluated regions, this mean is $6.72 \cdot 10^4$ and thus close to the above-mentioned overall mean. No difficulties arise for delimiting the individual regions in the

Table 5. Determination of calculatory increments for aromatic CH groups in the region of infrared spectroscopic gamma vibration bands

Substanz Substance	910–840 B_{z1}	840–780 B_{z2} (g/cm) · 10^{-4}	780–712 B_{z3}	712–650/cm^{-1} B_{z1}
2,3-Dimethyl-phenol			4,07	
2,5-Dimethyl-phenol	3,73	4,05		
3,5-Dimethyl-phenol	3,91			
3,4,5-Trimethyl-phenol	5,34			
2,4,6-Trimethyl-phenol	3,43			
3-Methyl-isoquinoline	4,67		3,52	
1-Naphthol		4,32	6,87	
2-Naphthol	(16,0)	6,15	4,43	
Fluorene			3,55	
2,3-Dimethyl-naphthalene	6,22		3,52	
1,2-Dihydroxy-tetralin			6,90	
Carbazole			7,52	
Diphenylene oxide			6,27	
Tetrahydrocarbazole			6,90	
2,3,6-Trimethylnaphthalene	5,30	3,66		
2-Äthoxy-naphthalene		5,46	3,10	
1-Hydroxy-2,6-dimethyl-naphthalene	9,50	4,11		
Anthracene	(14,38)		3,87	
Phenanthrene		(10,5)	3,71	
Acridine	(1,03)		5,28	
Phenanthridine	5,34		5,82	
9,10-Dihydro-anthracene			5,05	
4,4'-Dimethyl-diphenyl		3,87		
Diphenylene sulphide			5,84	
2,2'-Dihydroxy-diphenyl			6,65	
Octahydroanthracene	3,95			
2-Methyl-anthracene	8,05	3,76	6,21	
3-Methyl-phenanthrene	5,29	6,56	4,50	
2-Methyl-phenanthrene	7,36	5,79	6,85	
Anthrone			4,92	
Xanthone			4,93	
Fluoranthene		5,40	6,20	
1,2-Dihydropyrene		8,58	4,87	
2-Phenyl-naphthalene	10,2	4,65	8,31	(2,75)
Tetrahydro-fluoranthene			6,36	
Hexahydropyrene		5,34		
Phenanthrene-quinone			4,95	
4-Phenyl-(isopropyl)-phenol		5,03	5,03	4,68
4,4-Dihydroxy-diphenyl-1,1-ethane		5,37		
1,2-Benzo-fluorene		5,48	5,55	
2,3-Benzo-fluorene	7,95		5,35	
2,3-Benz-diphenylene oxide	(14,0)		5,58	
Triphenylene			5,75	
5,12-Dihydrotetracene	6,27		5,48	
2,2'-Dinaphthyl	12,94	10,7	3,35	
1,2-Benz-diphenylene sulphide		8,37	6,32	
4,4-Dihydroxydiphenyl-1,1-butane		5,00		
4,4-Dihydroxydiphenyl-1,1-cyclohexane		5,13		
4,4-Dihydroxydiphenyl-methyl-phenyl-methane		5,66		4,47
Biacenaphthylidene		5,65	5,65	
9,9'-Difluorenyl			5,24	

spectra of calibrating substances since the extinctions at the minima within the respective regions generally are small.

Even in the coal spectra a direct limitation of regions at the absorption minima is possible.

Deriving a method of group analysis for aromatic multicomponent mixtures

The most obvious manner of determining the statistical distribution of structural groups from data on pure substances is the one described below.

For the band complex in the region of 910-650 cm^{-1} we get the following equation for determining the percentages of aromatic hydrogen from the calculatory increment $B_{xCH_{ar}} = 6.75 \cdot 10^4$ (cm/g CH):

$$H_{ar} = \frac{B_{910-650}}{6.75 \cdot 10^4 \cdot 13} \cdot 100 = B_{910-650} \cdot 1.11 \cdot 10^{-4}. \qquad \text{(Equation 1)}$$

For calculating methyl group hydrogen the equation

$$H_{CH_3} = \frac{a_{1380}}{3.42 \cdot 10^2}$$

is transformed into

$$H_{CH_3} = \frac{a_{1380} \cdot 3}{4.32 \cdot 10^2 \cdot 15} \cdot 100 = a_{1380} \cdot 4.61 \cdot 10^{-2}. \qquad \text{(Equation 2)}$$

The hydrogen in phenolic hydroxyl groups was determined by a combined chemical/spectroscopic method described in greater detail elsewhere. Including the hydrogen content (H_{ges}*) determined by elemental analysis, we get the hydrogen in methylene and methine groups (H_{CH_2}):

$$H_{CH_2} = H_{ges} - (H_{ar} + H_{OH} + H_{CH_3}). \qquad \text{(Equation 3)}$$

---

* Translator's note: ges = total

The methylene and methyl group concentrations cannot be separated from each other by infrared spectroscopy alone. - This then accounts for all major hydrogen-containing structural groups, if we disregard a hydrogen fraction in other heteroatoms (—N—H; —S—H) which, although possible, will always be negligibly small.

The hydrogen concentrations in individual structural groups can be converted into the equivalent carbon percentages with the following equations:

Carbon in aromatic CH groups:

$$C_{CH\,ar} = 12 \cdot H_{ar} \qquad \text{(Equation 4)}$$

Carbon on phenolic hydroxyl groups:

$$C_{C-OH} = 12 \cdot H_{OH} \qquad \text{(Equation 5)}$$

The carbon contents in methylene and methine groups which cannot be separated from each other can be characterized by two boundary cases. In the first case we assume that only methine groups occur. Then

$$C_{CH} = 12 \cdot H_{CH} \qquad \text{(Equation 6b)}$$

In the following this will be called "Case b".

In the second case we assume that only methylene groups occur. Then

$$C_{CH_2} = 6 \cdot H_{CH_2} \qquad \text{(Equation 6a)}$$

In the following this will be called "Case a".

Carbon in methyl groups:

$$C_{CH_3} = 4 \cdot H_{CH_3} \qquad \text{(Equation 7)}$$

The organic carbon not determined by Equations 4-7 may occur either only in aromatics or as quaternary carbon in aliphatic groups. If we disregard the undoubtedly small fraction of quaternary carbon, the remaining aromatic carbon not linked with hydrogen or hydroxyl groups - if we include the carbon content determined by elemental analysis (C_{ges}) (waf basis) - is the following:

Case a) $C_{ar} = C_{ges} - (C_{CH_{ar}} + C_{C-OH} + C_{CH_2} + C_{CH_3})$ (Equation 8a)

Case b) $C_{ar} = C_{ges} - (C_{CH_{ar}} + C_{C-OH} + C_{CH_2} + C_{CH_3})$. (Equation 8b)

ges = total

From these values we can derive aromaticity, i.e. the relative carbon content in aromatic form, according to this Equation:

$$f_a = \frac{C_{CH_{ar}} + C_{C-OH} + C_{ar}}{C_{gesamt}} \qquad \text{(Equation 9)}$$

(gesamt = total)

Since we have disregarded quaternary carbon atoms, all calculated aromaticities may be slightly too high. Therefore, the aromaticities calculated according to Case a should be regarded as maximum values (f_a max), those calculated according to Case b, as minimum values (f_a min).

Examples of practical application

To conclude, Table 6 lists the results obtained with the above-described method for three seam coals from the Ruhr area. The coals in question are shown to be highly aromatic mixtures which, however, contain not inconsiderable aliphatic fractions. Extensive studies on coals and coal constituents will be described elsewhere.

Table 6. Group composition of selected seam coals

Zusammensetzung (1)		Kohle (% Flüchtige) (12)		
(2)		K (15)	K (28)	K (42)
Elementarzusammensetzung:	% C	91,26	87,80	75,34
	% H	4,32	5,54	5,25
	% O	3,06	5,02	13,01
Gruppenzusammensetzung (3)				
Anteil Kohlenstoff in: (4)				
aromatischen C-H-Gruppen (5)		21,4	17,3	13,3
Methylgruppen (6)		5,0	7,5	6,7
Methylengruppen (Fall a) (7)		10,6	16,9	21,6
Methingruppen (Fall b) (8)		21,6	34,0	43,0
(9) aromatisch gebundener Restkohlenstoff (Fall a)		62,4	56,3	52,4
aromatisch gebundener Restkohlenstoff (Fall b)		51,9	39,3	30,9
(10) Aromatizität (f_a max)		0,84	0,76	0,72
(f_a min)		0,74	0,70	0,70
(11) Verteilung der aromatischen Substitutionstypen:	% H1	33	41	33
	% H2	32	34	36
	% H3	30	22	27
	% H5	5	3	4

Key:
1 - composition
2 - elemental composition
3 - group composition
4 - percent carbon in:
5 - aromatic CH groups
6 - methyl groups
7 - methylene groups (case a)
8 - methine groups (case b)
9 - residual aromatic carbon (case a/b)
10 - aromaticity
11 - distribution of forms of aromatic substitution
12 - coal (% volatiles)

Experimental

Sample preparation. Potassium bromide and sample substance (approx. 0.5%) were ground under a vacuum (1 torr) in an agate ball mill for 480 min. 13-mm pellets were pressed from the mixtures, some of which were diluted.

Spectroscopy. All spectra were recorded with a 221 Perkin-Elmer spectrometer with NaCl windows. Ordinate extension was used only for weak bands. All measurements were compensated with an equivalent blank pellet.

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